



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :  C02F 1/46		(11) International Publication Number:  WO 98/12144
		(43) International Publication Date:  26 March 1998 (26.03.98)
<p>(21) International Application Number: PCT/GB97/02518</p> <p>(22) International Filing Date: 18 September 1997 (18.09.97)</p> <p>(30) Priority Data: 96118566/25 18 September 1996 (18.09.96) RU</p> <p>(71) Applicant (for all designated States except US): WILLOW-BANK TECHNOLOGIES LIMITED [GB/GB]; The Bindery, Eddington House Estate, Wantage Road, Nr. Hungerford, Berkshire RG17 0PL (GB).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): POPOV, Alexey Yurievich [RU/RU]; Solovini Proezd, 2-353, Moscow, 117593 (RU). POPOV, Dmitriy Alekseyevich [RU/RU]; Solovini Proezd, 2-353, Moscow, 117593 (RU).</p> <p>(74) Agents: VAUGHAN, Christopher, Tammo et al.; Haseltine Lake &amp; Co., Imperial House, 15-19 Kingsway, London WC2B 6UD (GB).</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b> With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</p>
<p>(54) Title: ELECTROLYTIC TREATMENT OF AQUEOUS SALT SOLUTIONS</p> <p>(57) Abstract</p> <p>There is disclosed a method and apparatus for generating a sterilising solution through the electrolytic treatment of aqueous salt solutions. A relatively concentrated aqueous salt solution (A) is passed, under pressure, into the working chamber (3) of an electrolytic cell (4), which cell is divided into a working chamber (3) and an auxiliary chamber (7) by a permeable membrane (5). At the same time, a relatively dilute aqueous salt solution (B) is passed through the auxiliary chamber (7). A proportion of the relatively concentrated solution (A) is filtered through the membrane (5), mixes with the relatively dilute solution (B), and the mixture is collected from an output of the auxiliary chamber (7). Gases, such as chlorine, liberated in the working chamber during electrolysis, are dissolved in a water supply (C), and this water supply is partially or fully mixed with the output of the auxiliary chamber (7) so as to generate a sterilising solution. The method and apparatus disclosed serves to generate a sterilising solution with less expenditure of energy and raw materials than in the prior art.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

-1-

ELECTROLYTIC TREATMENT OF AQUEOUS SALT SOLUTIONS

The present invention relates to a method and apparatus for the electrolytic treatment of aqueous salt solutions so as to generate solutions with oxidizing and/or reducing characteristics, and in particular, but not exclusively, to generate a sterilising solution.

It is known from GB 2253860, the disclosure of which is incorporated into the present application by reference, to treat water by passing this through an electrolytic cell having anode and cathode flow chambers separated by a permeable membrane, one of the chambers being a working chamber through which water to be treated passes in an upward direction, and the other being an auxiliary chamber, which is in closed communication with a gas-separating chamber located at a higher level than the electrolytic cell. Water having a higher mineral content than the water to be treated passes upwardly through the auxiliary chamber to the gas-separating chamber and recirculates to the auxiliary chamber by convection and by the shearing forces applied to the water through the rise of bubbles of gas which are generated on the electrode in the auxiliary chamber. The water pressure in the working chamber is higher than that in the auxiliary chamber, and gaseous electrolysis products are vented from the gas-separating chamber by way of a gas-relief valve.

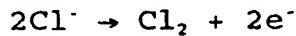
This method allows the pH value of the water being treated to be reduced from 7 to around 2 when the anode chamber is used as the working chamber. If instead the cathode chamber is used as the working chamber, the pH value of the water to be treated can be increased to around 12. This known method of electrolytic treatment is applied only to water having a relatively low concentration of dissolved salts and minerals (less

-2-

than  $10\text{gdm}^{-3}$ ), and the electricity supplied for the electrolytic treatment of water in the working chamber is only around 200 to  $3000\text{Cdm}^{-3}$ . Because the water to be treated has such a low concentration of dissolved salts and minerals, there is consequently a low concentration of useful electrolysis products (such as the chlorate (I) ion  $\text{ClO}^-$  which is produced when a sodium chloride solution is used in the auxiliary chamber and which acts as a disinfecting agent). In addition, water with a low concentration of salts and minerals tends to have a high ohmic resistance, which means that energy is used inefficiently when performing electrolysis. Furthermore, the small amount of electricity (200 to  $3000\text{Cdm}^{-3}$ ) applied to the water in the working chamber is insufficient to ensure the full transformation of the ions of dissolved salts (such as chloride ions  $\text{Cl}^-$ ) into useful electrolysis products (such as chlorate (I) ions  $\text{ClO}^-$ ). The incomplete electrolysis of dissolved salts means that a greater than theoretically necessary amount of salt must initially be dissolved in order to provide a required concentration of electrolysis products. This excess of dissolved salt can mean that the output of the electrolytic cell is overly corrosive, and when used as a disinfectant wash, tends to leave a coating of crystalline salt on surfaces which have been washed.

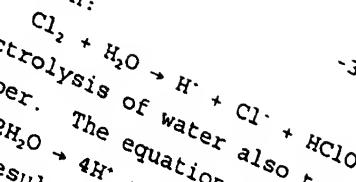
It is useful to consider the basic chemical reactions which take place in the anode and cathode chambers of the electrolytic cell. If the working chamber contains the anode, then the following reactions take place:

Chloride ions transform into gaseous chlorine in accordance with the following equation:



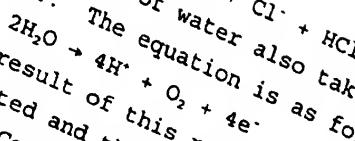
Gaseous chlorine dissolves in water and forms hypochlorous acid in accordance with the following

equation:



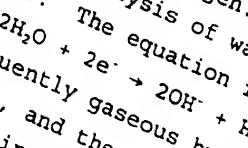
-3-

Electrolysis of water also takes place in the anode chamber. The equation is as follows:



As a result of this reaction, gaseous oxygen is liberated and the water becomes saturated with hydrogen ions. Consequently, the pH of the water falls in the anode chamber. The solubility of chlorine in the water reduces as the pH is lowered, and gaseous chlorine is liberated with oxygen.

Electrolysis of water takes place in the cathode chamber. The equation is as follows:



Consequently gaseous hydrogen is liberated at the cathode, and the concentration of hydroxide ions rises, thereby increasing the water pH in the cathode chamber. It follows from this analysis that the oxidizing ability of water is determined by the concentration of hypochlorous acid, and the reduction ability by the concentration of hydroxide ions. Water which has been under electrolytic treatment according to the method described in GB 2253860 has a low concentration of hypochlorous acid and hydroxide ions due to the low mineralisation of the initial water.

One way of estimating the effectiveness of a sterilising solution produced by the electrolytic treatment of a salt solution is to measure the concentration of "free chlorine", by which is understood the concentration of hypochlorous acid in water and the concentration of hypochlorite ion (formed by the dissociation of hypochlorous acid).

The concentration of free chlorine in water which has been treated in the anode chamber of the electrolytic cell of GB 2253860 does not usually exceed 0.2 to 0.6 gdm<sup>-3</sup>, although the solubility of gaseous

20

25

30

35

- 4 -

chlorine in water is much higher ( $7.3 \text{ gdm}^{-3}$  at  $20^\circ\text{C}$ ). It is therefore apparent that water which has been under electrolytic treatment in accordance with the known method has a concentration of free chlorine not more than 3 to 10% of the possible maximum.

According to a first aspect of the present invention, there is provided a method of treating aqueous salt solutions in an electrolytic cell, the cell comprising a working chamber and an auxiliary chamber separated from each other by a permeable membrane, one chamber including an anode and the other a cathode, wherein:

- i) a relatively concentrated aqueous salt solution is supplied under pressure to the working chamber;
- ii) a relatively dilute aqueous salt solution is supplied to the auxiliary chamber;
- iii) a proportion of the relatively concentrated solution is filtered under pressure through the permeable membrane into the auxiliary chamber so as to mix with the relatively dilute solution; and
- iv) an electric current is applied between the cathode and the anode through the aqueous salt solutions and the permeable membrane so as to cause electrolysis of the aqueous salt solutions.

According to a second aspect of the present invention, there is provided an apparatus for the electrolytic treatment of an aqueous salt solution, the apparatus comprising an electrolytic cell having a working chamber and an auxiliary chamber separated from each other by a permeable membrane, one chamber including an anode and the other a cathode, wherein, in use:

- i) a relatively concentrated aqueous salt solution is supplied under pressure to the working chamber;

-5-

ii) a relatively dilute aqueous salt solution is supplied to the auxiliary chamber;

5           iii) a proportion of the relatively concentrated solution is filtered under pressure through the permeable membrane into the auxiliary chamber so as to mix with the relatively dilute solution; and

10           iv) an electric current is applied between the cathode and the anode through the aqueous salt solutions and the permeable membrane so as to cause electrolysis of the aqueous salt solutions.

In a preferred embodiment, the working chamber includes the anode and the auxiliary chamber the cathode. The following description relates to this preferred embodiment, although it will be appreciated by a person of ordinary skill that the anode and 15 cathode may be reversed for certain applications.

Salts suitable for making up the aqueous salt solutions include sodium chloride, potassium chloride, lithium chloride and any combination thereof.

20           The electrolytic cell is advantageously configured so that the aqueous salt solutions pass in an upward direction. The working and auxiliary chambers may be defined by a concentric anode/cathode pair separated by the permeable membrane. The relatively concentrated 25 aqueous salt solution, which may typically contain 5 to 35% by weight dissolved salts, may be input to the bottom part of the working chamber, and partially output from the top part of the auxiliary chamber together with the relatively dilute aqueous salt 30 solution. In some embodiments, the concentration of salts in the relatively dilute aqueous salt solution may approach zero.

35           In contrast to the system disclosed in GB 2253860, the present invention may work on an aqueous salt solution with a relatively high concentration of dissolved salts (typically from 5 up to 35% by weight),

-6-

or even a saturated salt solution. This is passed under pressure into the working chamber, and is partially forced through the permeable membrane into the auxiliary chamber down the pressure gradient 5 between the two chambers. The flow rate of the aqueous salt solutions into the electrolytic cell may be set in such a way that the electricity requirement in the cell typically ranges from 30,000 up to 1,000,000Cdm<sup>-3</sup>.

The portion of the relatively concentrated 10 solution which passes out of the top of the working chamber, together with gases such as chlorine and oxygen (and possibly ozone and chlorine dioxide) which are liberated in the working chamber as a result of electrolysis, may be passed by way of a pressure regulator to a container where the liberated gases are 15 separated from the solution. The solution may be recycled through the working chamber of the electrolytic cell, and the liberated gases may be dissolved in a separate supply of water, for example by 20 way of a venturi, so as to impart oxidizing characteristics to this water. This allows gaseous chlorine to be dissolved in water so as to achieve considerably higher concentrations of free chlorine than in the method noted in GB 2253860. The solution 25 output from the auxiliary chamber, which has reducing characteristics, may be stored in a container and partially or fully mixed with the water with oxidizing characteristics, and may also be recycled through the auxiliary chamber. Gaseous hydrogen which is liberated 30 in the auxiliary chamber during electrolysis may be vented to atmosphere or passed to storage.

Embodiments of the present invention can generate aqueous solutions with oxidizing or reducing 35 characteristics and with a relatively high concentration of, for example, free chlorine or alkali, with considerably lower consumption of electricity and

- 7 -

salt feedstock than in the known system. This may be achieved by passing a relatively concentrated, and in some embodiments saturated, aqueous salt solution into the working chamber at a relatively low rate. The salt concentration is typically from 50 to 350gdm<sup>-3</sup>, which is 5 20 to 100 times higher than in the known system of GB 2253860, and the flow rate is typically 50 to 200 times lower. Because of the relatively high concentration of 10 the salt solution, its ohmic resistance is relatively low, which means that less electricity is required to perform the required electrolysis. The input into the working chamber is generally at a pressure greater than atmospheric pressure, which gives rise to a pressure drop across the membrane so that the greater part of 15 the solution passed into the working chamber is filtered through the permeable membrane into the auxiliary chamber. The magnitude of the pressure drop is typically in the range 0.02 to 0.15 MPa. This flow across the membrane helps to prevent hydroxide ions 20 from passing into the working chamber from the auxiliary chamber, and therefore allows a relatively low pH value (in some cases 1 or near to 1) to be maintained in the working chamber. Because the 25 solubility of gaseous chlorine is sharply reduced in a solution of low pH, this condition is very favourable for the liberation of gaseous chlorine in the working chamber.

The relatively low flow rate at which the 30 relatively concentrated aqueous salt solution is input to the working chamber means that the solution is heated to a relatively high temperature (undergoing a temperature rise of at least 10°C, and more preferably, at least 20°C) by the electric current passing between the anode and the cathode. A relatively high 35 temperature, for example 40°C, is also favourable for the liberation of gaseous chlorine, since the

-8-

solubility of gaseous chlorine in water at 40°C is less than half that at 10°C.

As discussed above, a relatively concentrated aqueous salt solution, which may be saturated, is supplied from the working chamber into the auxiliary chamber through a permeable membrane. In the working chamber, there is a relatively high concentration of Na<sup>+</sup> and H<sup>+</sup> ions, while in the auxiliary chamber, there is a relatively high concentration of hydroxide ions. Because of the low flow rate through the auxiliary chamber, the solution which is output from the auxiliary chamber has a high pH (typically from 11 up to 13), and is strongly alkaline.

When gaseous chlorine is dissolved in water, the pH of the water is lowered:



The lowering of the pH reduces the solubility of gaseous chlorine. To increase the concentration of free chlorine, some or all of the alkaline output of the auxiliary chamber of electrolyser is added to the water in which the gaseous chlorine is being dissolved so as to counteract the lowering of the pH and thereby to increase the solubility of gaseous chlorine. In this way, it is possible to achieve concentrations of free chlorine of 4gdm<sup>-3</sup> and higher, which is considerably greater (typically ten times greater) than the concentrations achieved by the method of GB 2253860.

Although the concentration of the initial aqueous salt solution used in the present invention is considerably higher than that used in GB 22253860, the low flow rate through the electrolytic cell means that overall salt consumption can typically be ten times lower. Furthermore, since the flow rate through the auxiliary chamber is low, the rate of deposition of hard salts, such as carbonates, on the cathode is also

low.

Should overheating of the electrolytic cell be observed, cooling water may be supplied to the auxiliary chamber. Furthermore, in order to remove any build-up of hard salts on the electrode in the auxiliary chamber, a detergent acid solution may be supplied to the auxiliary chamber in order to clear these deposits.

For a better understanding of the present invention, and to show how it may be carried into effect, reference shall now be made to the accompanying drawing, in which there is shown in schematic detail an embodiment of the present invention.

An aqueous salt solution A with a relatively high salt (e.g. NaCl) concentration is passed into a container 1. From here, the solution A is passed by way of a pump 2 into a working (anode) chamber 3 of an electrolytic cell 4, the working chamber 3 being bounded by a permeable membrane 5 and an anode 6. The greater part of the solution A then passes, under pressure, from the working chamber 3 via the permeable membrane 5 into an auxiliary (cathode) chamber 7, the auxiliary chamber being bounded by a cathode 8 and the permeable membrane 5. At the same time, an aqueous salt solution B with a relatively low salt concentration is passed, from bottom to top, through the auxiliary chamber 7 of the electrolytic cell 4. A potential difference is applied across the anode 6 and the cathode 8 so as to cause an electric current to pass through the solutions in the working chamber 3 and the auxiliary chamber 7, and through the permeable membrane 5. The flowing current causes an electrochemical transformation of the water and the salts dissolved in it in accordance with the equations given above. Due to the pressure difference across the membrane 5 established using a pressure regulator 10,

-10-

which pressure difference may be in the range from 0.02 to 0.15 MPa, a greater part of solution A seeps out of the working chamber 3 into the auxiliary chamber 7. Electrolysis gases formed in the working chamber 3, together with any of solution A which has not managed to seep through the membrane 5, emerge from the electrolytic cell 4 at the upper part of the working chamber 3, and arrive in the container 1 through a pipe 9 via the pressure regulator 10. Here the electrolysis gases are separated from the solution and are pumped from the container 1 through a pipe 11 by way of a venturi 12 and are dissolved in a water supply C so as to generate a solution with oxidizing properties. After passing through the venturi 12, the oxidizing solution arrives in a container 14 via a pipe 13, and is collected here for further use. If it is necessary to obtain a solution with a high concentration of oxidizing agents, such as hypochlorous acid, the solution is recycled a number of times through the venturi 12 by way of a pump 15 and a pipeline 16.

The solution A, having passed under the influence of the excess pressure from the working chamber 3 through the permeable membrane 5 into the auxiliary chamber 7 where it is mixed with solution B, becomes more concentrated with hydroxide ions and, having thereby acquired reducing properties, exits at the upper part of the auxiliary chamber 7 from the electrolytic cell 4 and enters a container 18 via a pipe 17. In the container 18, hydrogen liberated in the auxiliary chamber 7 is separated from the aqueous solution and led away to the atmosphere through a pipe 19. The aqueous solution may be recycled from the container 18 into the auxiliary chamber 7 via a pipe 20, while surplus solution is led out of the container 18 through a pipe 21. The solution from the container 18 may be added to the oxidizing solution in the

-11-

5 container 14, for example for the purpose of raising the pH value of the latter. This is done either by using a venturi 22 by way of a pipe 23 via a valve 24, or by using a dosing pump 25 by way of a pipe 26. The method illustrated in the Figure, in contrast to the known method, makes it possible to obtain an aqueous solution with oxidizing and reducing properties and a high content of active substances at a significantly lower consumption of raw material (salt) and electric  
10 power, and also to control within wide limits the pH value of the aqueous solution.

15 The values given above for the pressure difference across the permeable membrane 5 (0.02 to 0.15 MPa), for the concentration of salt in the water being fed into the working chamber 3 (5 to 35% by weight), and for the levels of specific consumption of electricity for  
electrochemically processing the water in the working  
chamber 3 (30,000 to 1,000,000Cdm<sup>-3</sup>), were determined by experiment.  
20

25 The greater the amount of electricity expended per unit volume of aqueous solution, the greater the efficiency of the electrolytic process. The concentration of salt in the aqueous salt solutions, the flow rate into the working chamber 3 and the current flow between the anode 6 and the cathode 8 all influence the electrolytic transformation of the aqueous salt solutions into the products of interest, such as gaseous chlorine and hypochlorous acid.

30 In the exemplary embodiment of the present invention, the flow rate of solution into the working chamber 3 is selected so that the specific expenditure of electricity is in the range between 30,000 to 1,000,000Cdm<sup>-3</sup>. At this level of expenditure, chloride ions in the relatively concentrated aqueous salt solution are almost fully transformed into gaseous chlorine.  
35

-12-

In the method of GB 2253860, a pH of 2 to 6 can be attained in the working (anode) chamber during electrolysis, but the solubility of gaseous chlorine in water at such pH levels is still relatively high.

5 In the exemplary embodiment of the present invention, on the other hand, a pH level near to 1 can be attained in the working chamber 3. At this level, the solubility of gaseous chlorine is considerably lower, which helps to promote the liberation of gaseous  
10 chlorine from the solution in the working chamber 3. This low pH level is achieved by passing the aqueous salt solution into the working chamber 3 under pressure greater than atmospheric, while maintaining atmospheric pressure in the auxiliary chamber 7. The resulting  
15 pressure drop across the permeable membrane 5 forces the solution to filter through the permeable membrane into the auxiliary chamber 7, thereby hindering the migration of hydroxide ions from the auxiliary chamber 7 into the working chamber 3. Because the hydroxide  
20 ions are kept within the auxiliary chamber 7, they are not able to neutralise the H<sup>+</sup> ions in the working chamber 3, and a low pH can therefore be maintained. In most cases, a pressure drop of 0.02 to 0.15 MPa across  
25 the permeable membrane 5 is enough to prevent the migration of hydroxide ions into the working chamber 3.

Because of the high specific expenditure of electricity in the exemplary embodiment of the present invention, the temperature of the solution in the working chamber 3 increases typically by 10 to 50°C. As  
30 the temperature of the solution rises, the solubility of gaseous chlorine is reduced, and the rate of liberation is consequently increased.

The solution which passes through the permeable membrane 5 from the working chamber 3 to the auxiliary chamber 7 has a high concentration of H<sup>+</sup> and Na<sup>+</sup> ions.  
35 In the auxiliary chamber 7, electrolysis of the

-13-

solution generates a surplus of hydroxide ions at the cathode:



The hydroxide ions react with the H<sup>+</sup> ions to form water:



Consequently, the solution in the auxiliary chamber 7 has a high concentration of hydroxide ions and Na<sup>+</sup> ions, and has a pH level typically in the range 11 to 13.

10           A specific example of the use of an embodiment of the present invention shall now be given, the results being compared with those achieved by the system disclosed in GB 2253860.

15           An electrolytic cell 4 was formed with an outer, cylindrical anode, made of titanium and coated on its inside surface with ruthenium oxide, and an inner, rod cathode, made of titanium, the anode and cathode being disposed concentrically. Between the anode and the cathode was placed a permeable ceramic cylinder made of zirconium oxide, with thickness 1mm and an effective filtration surface of 70cm<sup>2</sup>. The results of electrolytic treatment of an aqueous salt solution are presented in Table 1:

20

-14-

Table 1

	Present Invention	Prior art (GB2253860)	
5	Concentration of initial aqueous salt (NaCl) solution /gdm <sup>-3</sup>	300	3
10	Water flow rate through the working chamber/(dm <sup>3</sup> /hour)	0.1	18
15	Potential difference applied across the cell/V	4.0	18.0
20	Current supplied across the cell/A	15.0	15.0
25	Specific expenditure of electricity in the working chamber/Cdm <sup>-3</sup>	500,000	3,000
30	Concentration of free chlorine in the solution to which oxidising characteristics have been imparted/gdm <sup>-3</sup>	1.5	0.4
	Flow rate of water with oxidizing characteristics/(dm <sup>3</sup> /hour)	18	18
	Free chlorine productivity/(g/hour)	27	7.2
	Efficiency of conversion of sodium chloride to free chlorine/(g[ClO <sup>-</sup> ]/g[NaCl])	0.90	0.12
	Power consumption of the electrolytic cell/(kWh)	0.12	0.27
	Specific power consumption (required to generate 1kg of free chlorine/(kWh/kg)	6.6	37.5

-15-

It can be seen that this embodiment of the present invention has the following advantages over the prior art:

- 5        i)    180 times less water is passed through the working chamber, which greatly reduces carbonate deposition on the cathode.
- 10      ii)   The amount of free chlorine produced and the effective concentration in the sterilising solution is 3.75 times higher.
- 15      iii)   The efficiency of conversion sodium chloride sodium into free chlorine is 7.5 times higher.
- iv)   The electric power used in the electrolytic cell is halved.
- v)   The electric power required to generate 1kg of free chlorine is 5.7 times lower.

CLAIMS:

1. A method of treating aqueous salt solutions in an electrolytic cell, the cell comprising a working chamber and an auxiliary chamber separated from each other by a permeable membrane, one chamber including an anode and the other a cathode, wherein:

5           i) a relatively concentrated aqueous salt solution is supplied under pressure to the working chamber;

10          ii) a relatively dilute aqueous salt solution is supplied to the auxiliary chamber;

15          iii) a proportion of the relatively concentrated solution is filtered under pressure through the permeable membrane into the auxiliary chamber so as to mix with the relatively dilute solution; and

20          iv) an electric current is applied between the cathode and the anode through the aqueous salt solutions and the permeable membrane so as to cause electrolysis of the aqueous salt solutions.

2. A method according to claim 1, wherein the working chamber includes the anode and the auxiliary chamber includes the cathode.

3. A method according to claim 1 or 2, wherein the relatively concentrated aqueous salt solution is made up from water and at least one salt selected from the group comprising: sodium chloride, potassium chloride and lithium chloride.

4. A method according to any preceding claim, wherein the concentration of salt in the relatively concentrated aqueous salt solution is from 5 to 35% by weight.

35          5. A method according to any one of claims 1 to 3, wherein the concentration of salt in the relatively concentrated aqueous salt solution is in the range 50 to 350 gdm<sup>-3</sup>.

-17-

6. A method according to any one of claims 1 to 3, wherein the relatively concentrated aqueous salt solution is a saturated solution.

5 7. A method according to any preceding claim, wherein the aqueous salt solution is supplied at a pressure such that there is a pressure drop of 0.02 to 0.15 MPa across the permeable membrane.

10 8. A method according to any preceding claim, wherein the electricity supplied to the aqueous salt solutions is in the range 30,000 to 1,000,000 Cdm<sup>-3</sup>.

15 9. A method according to any one of claims 2 to 8, wherein gases evolved at the anode in the working chamber are taken from the working chamber and dissolved in a supply of water so as to generate a solution with oxidizing characteristics.

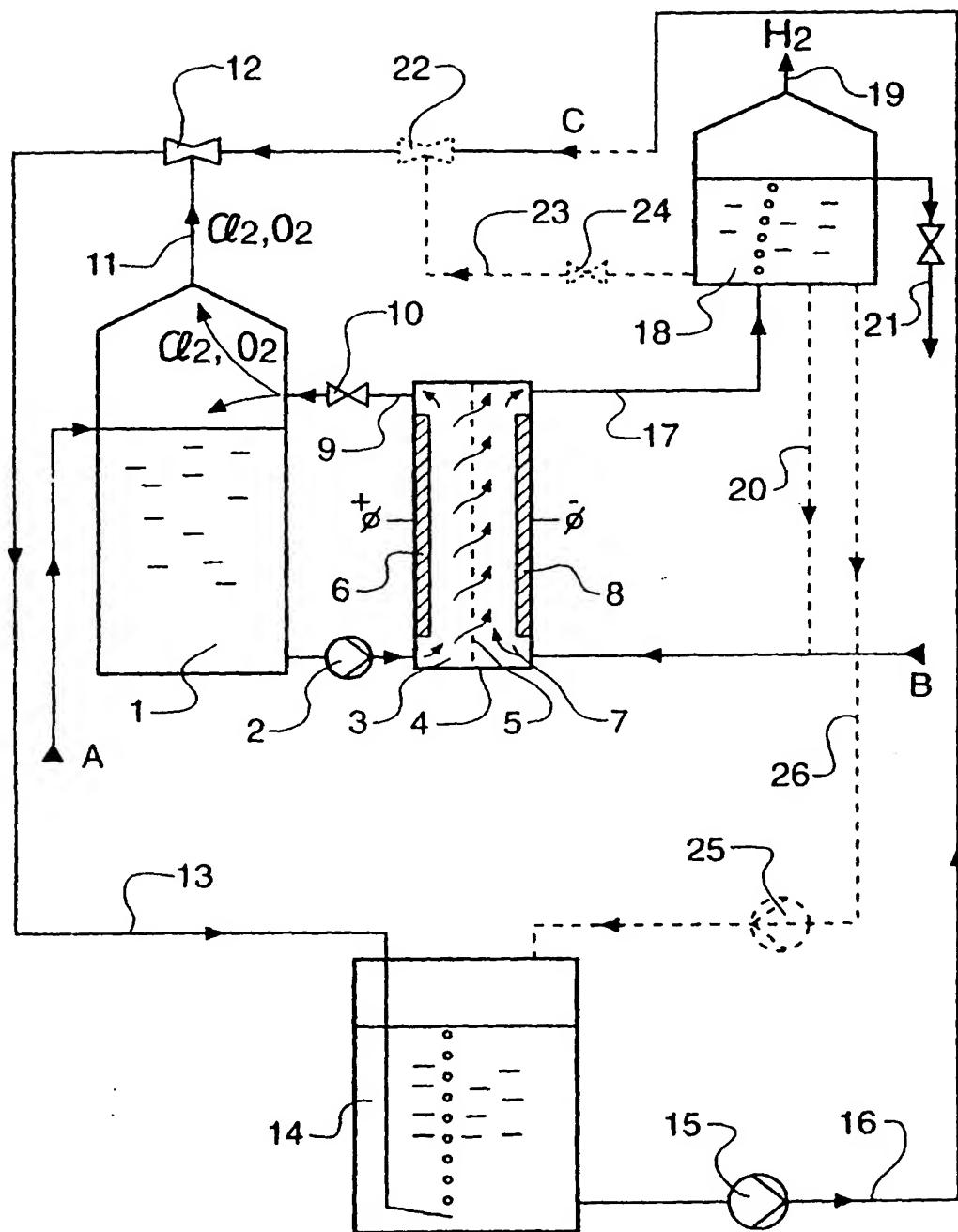
20 10. A method according to claim 9, wherein the water supply and/or the solution with oxidising characteristics is mixed in a predetermined ratio with the solution passed out of the auxiliary chamber so as to form a sterilising solution.

25 11. A method according to any preceding claim, wherein the proportion of relatively concentrated aqueous salt solution which does not pass through the permeable membrane is output from and recycled into the working chamber.

30 12. A method according to any preceding claim, wherein the electric current causes the temperature of the solution in the cell to rise by at least 10°C above the temperature of the solution initially supplied to the cell.

35 13. An apparatus for the electrolytic treatment of an aqueous salt solution, the apparatus comprising an electrolytic cell having a working chamber and an auxiliary chamber separated from each other by a permeable membrane, one chamber including an anode and the other a cathode, wherein, in use:

- i) a relatively concentrated aqueous salt solution is supplied under pressure to the working chamber;
  - ii) a relatively dilute aqueous salt solution is supplied to the auxiliary chamber;
  - 5           iii) a proportion of the relatively concentrated solution is filtered under pressure through the permeable membrane into the auxiliary chamber so as to mix with the relatively dilute solution; and
  - 10          iv) an electric current is applied between the cathode and the anode through the aqueous salt solutions and the permeable membrane so as to cause electrolysis of the aqueous salt solutions.
14. An apparatus as claimed in claim 13, wherein the working chamber includes the anode and the auxiliary chamber includes the cathode.
15. An apparatus as claimed in claim 13 or 14, wherein the permeable membrane is made from a ceramic material.
20. An apparatus as claimed in claim 13, 14 or 15, wherein the permeable membrane is made from zirconium oxide.
25. An apparatus as claimed in any one of claims 13 to 16, wherein a gas/liquid separator is connected to an output of the working chamber of the cell.
18. An apparatus as claimed in any one of claims 13 to 17, wherein a gas/liquid separator is connected to an output of the auxiliary chamber of the cell.
30. A sterilising solution produced by the method of claim 10.



# INTERNATIONAL SEARCH REPORT

Int'l. Application No  
PCT/GB 97/02518

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C02F1/46

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 427 667 A (BAKHIR VITOLD M ET AL) 27 June 1995 see column 2, line 50 - column 6, line 68; figures 3A,7 see examples 1-4	1,2,7,9, 13-19
A	---	3-6,8, 10-12
X	GB 2 257 982 A (KIRK AND COMPANY INTERNATIONAL) 27 January 1993 see page 1, paragraph 3 - page 3, paragraph 3; figure 1	1,2,9, 13,14,19
X	GB 2 253 860 A (KIRK AND CHARASHVILI INTERNATI) 23 September 1992 cited in the application see page 4, paragraph 4 - page 17, paragraph 1; figure 1	1,2, 9-11, 13-19
A	---	3-7,12
		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

- 'A' document defining the general state of the art which is not considered to be of particular relevance
- 'E' earlier document but published on or after the international filing date
- 'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- 'O' document referring to an oral disclosure, use, exhibition or other means
- 'P' document published prior to the international filing date but later than the priority date claimed

- 'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- 'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- 'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- 'S' document member of the same patent family

Date of the actual completion of the international search

10 December 1997

Date of mailing of the international search report

16.01.98

Name and mailing address of the ISA  
European Patent Office, P.B. 5818 Patenttaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl  
Fax: (+31-70) 340-3016

Authorized officer

Assogna, R

## INTERNATIONAL SEARCH REPORT

Int'l. Appl. No.  
PCT/GB 97/02518

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT	
Category	Citation of document, with indication, where appropriate, of the relevant passages
A	US 5 540 819 A (BAKHIR VITOLD M ET AL) 30 July 1996 ---
A	US 4 048 032 A (EIBL VOLKER) 13 September 1977 -----

1

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

Int'l Application No

PCT/GB 97/02518

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5427667 A	27-06-95	RU 2038322 C RU 2040477 C RU 2038323 C RU 2042639 C DE 4391418 T GB 2274113 A,B JP 7509536 T WO 9320014 A	27-06-95 25-07-95 27-06-95 27-08-95 05-05-94 13-07-94 19-10-95 14-10-93
GB 2257982 A	27-01-93	NONE	
GB 2253860 A	23-09-92	NONE	
US 5540819 A	30-07-96	RU 2064440 C DE 4318628 A GB 2267508 A,B JP 6134465 A	27-07-96 09-12-93 08-12-93 17-05-94
US 4048032 A	13-09-77	DE 2442078 A AR 206934 A BR 7505642 A EG 11803 A FR 2283698 A GB 1507324 A JP 51052648 A OA 5097 A	18-03-76 31-08-76 15-03-77 31-03-79 02-04-76 12-04-78 10-05-76 31-01-81